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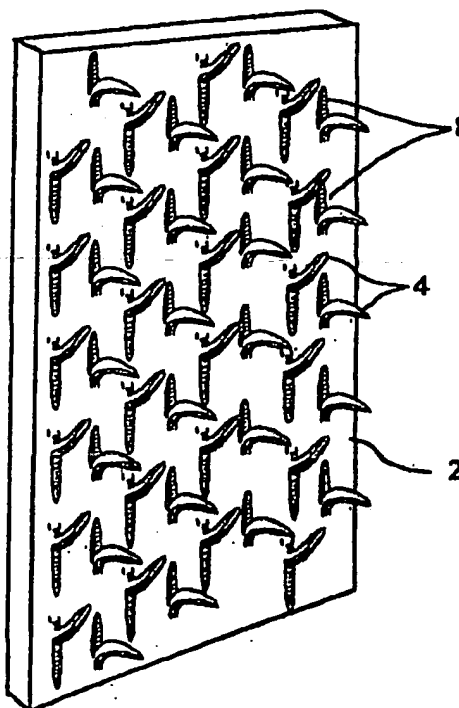
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(54) Title: **ELECTRODES FOR BATTERIES AND OTHER ELECTROCHEMICAL DEVICES**

(57) Abstract

An electrically conductive first component (2) of an electrochemical cell is formed at a surface with protruding tongues or flanges (4) extending through a transition zone into an adjacent parallel second component (6) of the cell such as a layer of active material so as to present surfaces (5, 7) to the material of the second component in the transition zone which face both forwards and away from the surface of the first component so as to improve the physical, electrical and thermal interaction of the components and distribute that interaction through the transition zone.



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ELECTRODES FOR BATTERIES AND OTHER ELECTROCHEMICAL DEVICES

This invention relates to electrode components for use in electro chemical cells such as primary and secondary batteries, fuel cells and the like, in which an electrode
5 component is located adjacent a further parallel component of the cell, typically a layer of active material.

In this specification, the term "electrode components" is used in a broad sense to apply not only to electrodes in the sense of material forming an electrochemically active pole of
10 a cell, but also to structures such as plates or cans not themselves consisting of active material but supporting or contacting such active material and forming current collectors for such cell poles. The term 'parallel', as used in relation to components of cells, is used to indicate that
15 the components extend so that their surfaces are generally equidistant, and although generally planar surfaces may be described and illustrated, it should be understood that the surfaces may be curved or otherwise shaped to suit the structure of the cell in which the components are employed.

20 The further component of the cell may be an active material forming the electrode proper, or an active mass or other layer performing some other function such as a depolariser or permeable separator.

An important characteristic of such electrode components,
25 particularly the current collectors of cells, is their effective surface area, which in many cases should be as large as possible consistent with desired mechanical and electric current carrying capabilities of the electrode. Additionally, many battery and electrochemical cell
30 structures that require that the current collector be in intimate contact with a further layer of active material, often of much less mechanical strength than the collector itself. It is usually important both that the combined structure retain effective mechanical, electrical and thermal

contact with the layer of active material, and present and maintain the greatest possible contact area with that layer.

It is known for example to form the electrodes or plates of lead-acid batteries in the form of current collector grids, 5 which support active material or paste to form battery plates. In other battery constructions, electrodes formed of expanded metal have been used, in view of their enhanced surface area and their ability to retain active material within the expanded metal mesh. In the collector cans of 10 battery and other cells, it is known to treat the interior surface of the cans with a view to increasing their surface area, and/or to provide a desirable distribution of discrete active areas or sites.

In United States Patent No. 5,376,410 (MacKelvie), there is 15 disclosed a technique for surface modification of a material to improve its adhesion to another material in a mechanical and/or adhesive bonding process. This process involves applying a planing action to multiple points on the surface of a material to be treated, to raise undetached shavings 20 forming tongues or flanges extending out of the surface of the material.

It has now been found that this and similar types of surface modification treatment, and the type of surface so formed, may advantageously be applied to conductive material utilized 25 in the construction of electrode components of electrochemical cells such as battery cells, in that the treatment enables establishment of a transition zone between the surface modified component and a second component of the cell extending beyond the tongues or flanges, within which 30 zone the contact area between the components is increased, and a desirable mechanical, electrical and thermal coupling occurs between the components.

According to the invention, an electrode of an electrochemical cell comprises a first component of

conductive material presenting a surface having an array of separate elongated channels formed in the surface of the component without penetrating it, and an array of integral tongues or flanges rooted adjacent the channels and extending
5 away from the surface so as to present surfaces facing both towards and away from the surface, and a second component extending generally parallel to the first component, the tongues or flanges engaging material forming the second component in a transition zone without extending beyond said
10 second component, such as to provide a physical, electrical and thermal coupling between the components.

At least the surface material of the first component may be of metal or conductive plastics material, capable of being formed to provide the channels and non-detached tongues or
15 flanges.

Depending on the type of cell involved, the first component surface may be surface coated with a catalyst or other active material distinct from the cell component supported by the tongues or flanges so as to provide the first component
20 with desired surface properties.

In one embodiment of the invention, the first component surface is formed both with channels in which are rooted tongues as defined above, and also with a second pattern of similar channels and tongues of substantially larger
25 dimensions and spacing whereby further to increase the electrode surface.

The invention is described further with reference to the accompanying drawings in which:

Figure 1 shows an electrode component of an electrochemical
30 cell in accordance with the invention;

Figure 2 is a cross section through an electrode component similar to that of Figure 1, to which has been applied a

layer of active material; and

Figure 3 is a fragmentary cross sectional view illustrating how two series of cuts of widely different dimensions may be formed on the surface of the same electrode component.

- 5 The present invention, according to the type of cell in which it is applied, provides electrode components with enhanced performance in several distinct respects, in that it increases the active surface area of the electrode component, and also establishes a transition zone between the electrode
10 component and an adjacent component of the cell extending generally parallel to its surface. The second characteristic can be exploited not only in those cases where a layer of active material is in direct contact with the surface of the electrode component, such an arrangement being a common
15 feature of primary and secondary battery cells, and other electro chemical cells, but also when a contact zone of defined characteristics is required between the component surface and an adjacent parallel component of the cell.

Referring to Figure 1, there is shown a plate 2 of conductive
20 material such as a metal suited to the type of cell to be constructed, or a conductive synthetic plastic resin. In either case, the metal or resin is selected to be freely machinable such that its surface may be treated by a suitable tool, for example as described in U. S. Patent No. 5,376,410,
25 or using a tool as described in Canadian Patent No. 1,337,622, to provide a configuration similar to that of Figure 1, in which a number of non-detached cuttings or tongues 4 have been planed out of the material surface by planing cuts terminated prior to completion. These cuttings
30 or tongues are rooted at the one end of channels from which they are planed, and are curved away from the material surface. The result of the presence of the cuttings is that the area of the surface is increased by an amount approximately equal to double the surface area of the
35 channels 8. If a layer of active material 6 is formed

adjacent the plate (see Figure 2), the tongues provide an excellent physical bond to the material, and improve the electrical and thermal coupling between it and the plate surface not only through the increased surface area but
5 because of the penetration of the tongues into the active material 6, and the fact that the tongues present surfaces facing both towards and away from the surface. This means that any tendency of the material to move away from a surface will be accompanied by a corresponding tendency to press
10 against an oppositely facing surface, while the tongues can flex to help maintain good physical, electrical and thermal contact. Since the interface between the cell components is distributed through a zone 9 of finite thickness, physical and electrical stress concentrations are reduced, and the
15 resistance across the interface can also be reduced.

If appropriate to the function of the cell in which an electrode is to be used, the electrode structure surface may be coated or plated with a thin surface layer of a further active material, for example, platinum acting as a catalyst,
20 either before or after formation of the tongues.

Referring now to Figure 3, this shows how two series of planing cuts of different dimensions may be applied successively to the same surface in order to further increase its surface area and ability to bond active material. A
25 first, series of small cuttings 4A is made in the surface as shown in Figure 1, and then a second series of much larger cuttings 4B is made in the same surface so that some of the cuttings 4A extends from the surface of the cuttings 4B.

The foregoing embodiments of the invention are applicable to
30 any electrode material that is sufficiently freely machinable that planing cuts which are terminated without completion will raise cuttings or shavings which remain intact and attached to the substrate material at the point of termination of the cut, and which is electrically conductive.
35 This includes material whose machining properties are

asymmetric; for example, materials of fibrous structure may be sufficiently machinable along the grain of the porous structure but not across it. Other materials may only be adequately machinable if the cut is shallow enough that the cut or shavings are not subjected to excess bending stresses as they are planed from the surface. These factors should be taken into account when selecting materials and cutting or planing parameters. The electrode material is not necessarily metallic. Electrically conductive synthetic resins with suitable machining properties may be used, and some forms of graphite may be suitable. The electrode material is not necessarily in sheet form; any electrode structure or element presenting a planable surface, for example a rod or the inside or outside surface of a cylinder may be processed. One or both surfaces of a sheet or plate form electrode may be processed. The electrode may comprise a film or layer of machinable material supported on a substrate, or may have a layered or composite structure, provided that the material is machinable as described. In the case of a material that is susceptible to moulding or casting, but not necessarily readily machinable, it may be preferred to provide a prototype component formed of readily machinable material, and use this as a matrix to form a mould used to cast the actual component. For casting to be practicable, the form of surface modification and the mould and component materials must be such as to permit the casting to be removed from the mould.

In a cell such as an alkaline manganese primary cell, it will normally be desirable to optimize the contact area and mechanical bonding between a current collector such as a cell can, and active material such as manganese dioxide mixed with carbon and forming the electrode proper, in the manner shown in Figure 2. Tests have shown that application of the invention can lead to significantly improved performance in such cells.

In order to provide suitable support for the other component, the tongues may be dressed if necessary in various ways to provide a suitable support surface. For example, the projecting tongues may be lightly pressed to provide a controlled degree of projection, or abraded to remove sharp projections.

In some structures, the tongues may be formed with different heights so as to extend different distances into the adjacent layer. The tongues may also spiral from the surface and cork-screw depending on the material employed and the cutting action utilized. In some cell structures, it may be desirable for the electrode surface to present an array of discrete islands or "sites" where electrochemical action takes place. This is readily arranged with electrode structures of the invention by applying an insulative layer to the surface of the treated electrode structure so that only the raised tongues protrude through the insulative layer into a layer of active material.

Tests on a sample of lead treated using the technique of the invention have established that an increase in geometric surface area to 200% of that of a sample not so treated can be achieved. Since an increase in geometric surface area does not necessarily provide an equivalent increase in effective electrochemical surface area, additional testing may be required to establish the latter for any particular type of cell. Measurements of increase in effective electrochemical surface area were made on electrode comprising a carbon loaded conductive polymer in a cell formed by the carbon/polymer electrode and a zinc electrode in 9 molar aqueous potassium hydroxide solution. 1 cm² nominal surface area (i.e., ignoring surface texture) polymer electrodes were used, with the backs of the electrodes pressed against a nickel grid and embedded in insulative epoxy resin. The active surface area of the electrodes was measured by determining the capacitative response of the cell at different frequencies, thus enabling the double layer

capacity of the electrode under test to be isolated and determined. Untreated carbon/polymer electrodes were tested, together with two otherwise similar electrodes whose exposed surface had been subjected to different patterns of planing cuts, using available tools developed for other purposes. One of these samples showed an increase of 7% in effective electrochemical surface area and the other an increase of 21%. Since the effective electrochemical area of the untreated electrode was estimated to be some four times its nominal surface area, possibly due to porosity or texture of the electrode surface, the percentage increase in effective electrochemical surface area relative to nominal surface area is substantially greater than the figures quoted above, and this in spite of the absence of any optimization of the size, shape and distribution of the cuttings on the treated electrodes. Tests have also been carried out on relatively thin films of carbon/polymer material, and it is found that such films can be successfully surface treated, provided that the depth of the planing cuts is controlled to a magnitude substantially less than the thickness of the film. For example, planing cuts 0.04 mm deep have successfully been formed in the surface of film 0.125 mm thick. It should be understood that the planing cuts should not in any embodiment of the invention penetrate through the electrode component being treated.

The invention is seen as having particular utility in electrodes for primary battery cells, such as carbon/zinc cells and alkaline manganese cells wherein it is usually desirable to maximize the effective electrochemical surface area of the current collectors, and fuel cells, but it may be used in any electrochemical cell to increase the effective area of one or both electrodes and optimize support of adjacent active material in the electrode structure, provided that the electrode comprises, or has a conductive substrate comprising, a material which is sufficiently ductile for material gouged from cuts in its surface to form tongues or flanges raised from the surface but remaining attached to the

surface adjacent the cuts. Since the material of the current collector or other surface modified electrode component is merely displaced, the volume available for the adjacent cell component remains unchanged, thus avoiding loss of volumetric efficiency.

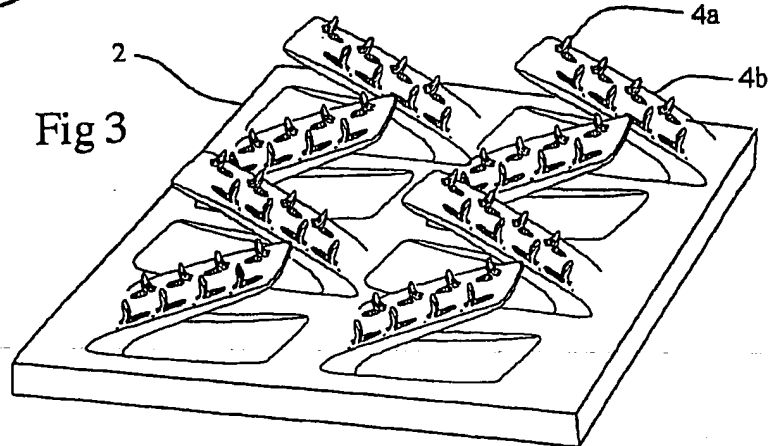
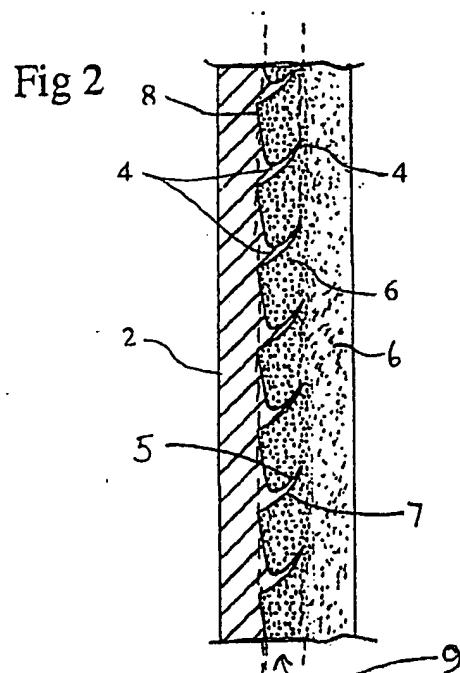
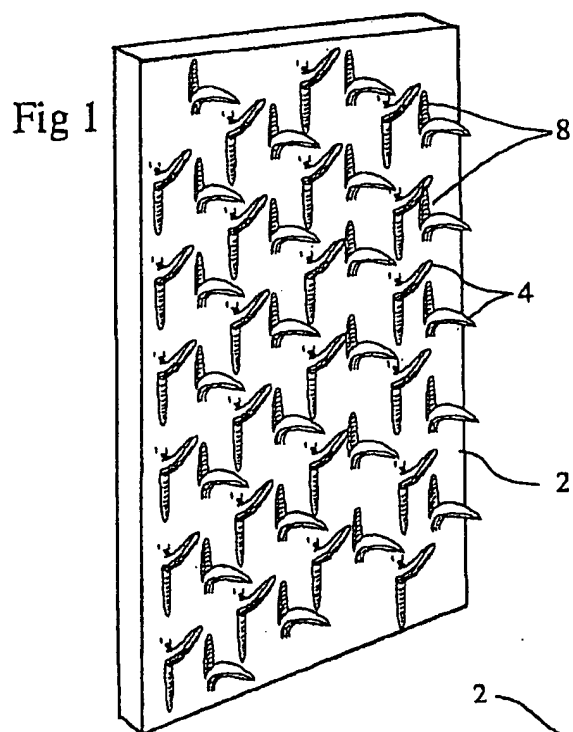
Although the invention has been described with particular reference to a surface modification process as described in U.S. Patent No. 5,376,410, it should be understood that other forms of surface modification may be used provided that they result in material of the component whose surface is being modified being formed into a suitable array of tongues or flanges adjacent the channels. For example, the surface of the material may be ploughed by suitable cutting elements so as to raise material from the channels and displace it to form tongues or flanges extending to one or both sides of the channels. The pattern of surface modification may be modified both by controlling the distribution of the cutting elements, or by selectively pressing, dressing or machining the tongues or flanges once formed. In any event, the tongues or flanges need to present surfaces facing both towards and away from the component surface so as to be embedded in the other component to achieve the desired enhanced electrical, physical and thermal contact through the transition zone.

CLAIMS

- 1) An electrode of an electrochemical cell characterized in that it comprises a first component (2) of conductive material presenting a surface having an array of separate elongated channels (8) formed in the surface of the component without penetrating it, and an array of integral tongues or flanges (4) rooted adjacent the channels and extending away from the surface so as to present surfaces (5,7) facing both towards and away from the surface, and a second component (6) extending generally parallel to the first component, the tongues or flanges engaging material forming the second component in a transition zone (9) without extending beyond said second component, such as to provide a physical, electrical and thermal coupling between the components.
- 2) An electrode according to claim 1, characterized in that the first component (2) is of metal.
- 3) An electrode according to claim 1, characterized in that the first component (2) is of electrically conductive synthetic resin.
- 4) An electrode according to claim 3, characterized in that the first component (2) is of carbon bonded with synthetic resin.
- 5) An electrode according to any of claims 1-4, characterized in that the first component (2) is a current collector, and the second component (6) is a layer of active material in which the tongues or flanges are embedded.
- 6) An electrode according to claim 5, wherein the layer (6) of active material is a mixture of manganese dioxide and carbon.

- 7) An electrode according to any of claims 1-5, characterized in that the electrode surface is formed both with channels and tongues or flanges (4a) as defined above, and also with a second pattern of cuts of substantially larger dimensions and spacing providing a much larger scale series of channels and tongues or flanges (4b) whereby further to increase the electrode surface.
- 8) An electrode according to any of claim 1-7, characterized in that the first component (2) has an array of separate elongated channels (8) formed into its surface without penetrating the component, with a non-detached raised, elongated tongue (4) rooted at one end of each channel and springing from it initially in line with the channel and away from its surface.
- 9) An electrochemical cell incorporating at least one electrode according to any of claims 1-8.
- 10) A cell according to claim 9, wherein the cell is a primary battery cell.

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INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/CA 97/00841

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01M4/70 H01M4/02 H01M4/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 130 917 C (O.R. SCHULZ) 5 June 1902 see the whole document ---	1-6,8-10
Y	US 5 376 410 A (MACKELVIE WINSTON R) 27 December 1994 cited in the application see the whole document ---	1-6,8-10
A	DE 35 396 C (ELECTRICITEITS MAATSCHAPPIJ SYSTEEM DE KHOTINSKY) 30 April 1886 see claim 1 ---	1-10
A	FR 429 054 A (H.P.R.L. PÖRSCKE, J.A.E. ACHENBACH) 14 September 1911 see claims 1-3 ---	1-10
A	DE 91 01 872 U (G. SCHÖLL) 30 July 1992 see claims 1,2 ---	1-10
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 1 033 177 A (O. WELTER) 8 July 1953 see claims 1,2 ---	1-10
A	FR 429 424 A (C. TAILHANDIER DU PLAIX) 22 September 1911 see claim 1 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

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